



Short communication

Optimization of an anode fabrication method for the alkaline Direct Formate Fuel Cell

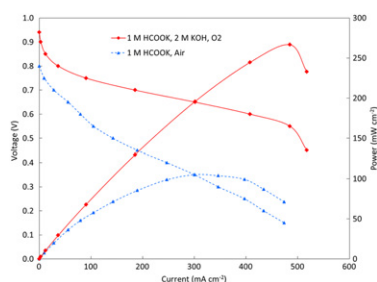
Amy M. Bartrom, Jennine Ta, Tien Q. Nguyen, John Her, Alexandra Donovan, John L. Haan*

Department of Chemistry and Biochemistry, California State University, 800 N State College Blvd, Fullerton, CA 92834, USA

HIGHLIGHTS

- We show significantly improved performance in a Direct Formate Fuel Cell.
- This fuel cell produces power density greater than other alkaline liquid fuel cells.
- This fuel cell still produces competitive power without KOH and using air as oxidant.
- The alkaline environment is advantageous for catalysts and reaction rates.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 July 2012

Received in revised form

16 November 2012

Accepted 2 December 2012

Available online 10 December 2012

Keywords:

Potassium formate

Formate oxidation

Direct liquid fuel cell

Alkaline membrane

Anion exchange membrane

ABSTRACT

The performance of an alkaline Direct Formate Fuel Cell (DFFC) employing a polymer anion exchange membrane has been greatly improved by optimization of the method and amount of catalyst loading at the anode. An optimum anode for this DFFC was obtained by a combination of direct-membrane spray painting and gas diffusion layer brush painting. When this fuel cell was operated at 60 °C with 1 M HCOOK, 2 M KOH, and oxygen, its current density at 0.6 V was 408 mA cm⁻², and its maximum power density was 267 mW cm⁻². When KOH was removed from the fuel stream, a power density of 157 mW cm⁻² was achieved. Both of these power densities are very competitive with recent reports of alkaline direct liquid fuel cells (DLFC). We also demonstrate the DFFC when air was used at the cathode and no KOH was added to the fuel; the maximum power density was 105 mW cm⁻² in this case.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Direct liquid fuel cells (DLFCs) are being commercialized for use in portable electronic devices due to their high energy density [1–3]. Optimized DLFCs afford simple, liquid storage for the fuel and an air-breathing cathode for the oxidant. The majority of DLFCs employ acid chemistry, in which protons are conducted across a Nafion® polymer electrolyte membrane from anode to cathode.

However, the recent development of alkaline anion exchange membranes, which conduct hydroxide ions from cathode to anode, has renewed interest in the application of alkaline chemistry to DLFCs [4–11].

Within the past year, there have been two demonstrations of a Direct Formate Fuel Cell (DFFC), which uses dissolved potassium formate as the fuel. Jiang and Wieckowski demonstrated a DFFC which could produce 170 mW cm⁻² at 120 °C with 6 M HCOOK and 2 M KOH using a polybenzimidazole-based membrane [12]. Bartrom and Haan demonstrated an alkaline DFFC which produced the following maximum power densities at 60 °C using a Tokuyama A201 membrane: [13].

* Corresponding author. Tel.: +1 6572787612; fax: +1 6572785316.

E-mail address: jhaan@fullerton.edu (J.L. Haan).

- 1) 144 mW cm⁻² using 1 M HCOOK, 2 M KOH, and oxygen
- 2) 125 mW cm⁻² using 1 M HCOOK, 2 M KOH, and air
- 3) 51 mW cm⁻² using 1 M HCOOK and oxygen

Our report also demonstrated that the formate oxidation rate does not degrade overnight in an electrochemical cell, suggesting stability for the catalyst and the reaction rate. In addition, the membrane used in our study has been demonstrated recently to possess long-term stability; the small rate of performance decline with time was attributed primarily to slow anode catalyst degradation due to particle size growth [14].

Until this year, ethanol was the leading fuel reported for alkaline DLFCs in terms of power density; ethanol is also a very attractive fuel from a viewpoint of renewability [5,6,11]. The use of ethanol was impractical in an acid fuel cell, but several reports have demonstrated the viability of the alkaline direct ethanol fuel cell (DEFC), and its best performance at 60 °C was shown to be 185 mW cm⁻² when assembled with a polymer anion exchange membrane [6–9,11]. Although it is still difficult to oxidize ethanol completely to carbon dioxide, it partially oxidizes more readily than in an acid environment, making it a viable candidate for the fuel of an alkaline DLFC [15]. However, formate is also an interesting fuel for alkaline DLFCs for a variety of reasons. Formate is known to oxidize readily on palladium at a lower potential than ethanol without formation of catalyst poison [16–18]. The theoretical cell voltage is 1.45 V, which is greater than that of DLFCs employing alcohol fuels. Formate salts have advantages for storage and transportation, and they are already approved for use in the environment [19]. There is also potential for formate to be produced as a renewable fuel from the reduction of carbon dioxide [20–22]. Formate is also of interest on a fundamental surface science level. Researchers are investigating the possible role of formate as an intermediate in the oxidation of methanol in alkaline environments. Methanol is another small organic fuel with the potential to be used in alkaline DLFCs, but its oxidation mechanism is complex. Formate is of particular interest in methanol oxidation due to its role as a surface species which is competitive with the strongly adsorbed CO intermediate [4,10].

In this paper, we report on: 1) steps taken at the anode in order to optimize the DFFC from our first report and 2) electrochemical measurements in which we seek to answer questions about the anode reaction and its relevance to overall performance of the DFFC. We report a significantly higher power density in all fuel and oxidant configurations. We attempt to draw correlation between the dependence on fuel concentration, KOH concentration, and temperature between the fuel cell and an electrochemical half cell. We also demonstrate the possibility of employing the DFFC under conditions of no alkaline KOH in the fuel stream and air at the cathode; this key condition has not yet been reported to our knowledge for an alkaline DFFC.

2. Experimental

2.1. Fuel cell

The fuel cell assembly and testing procedure are the same as previously described [13] except for the following modifications. The palladium black anode catalyst was spray painted directly onto the A201 membrane using a 2 × 2 cm template which produced an active area of 4 cm². This spray painting technique produces a more uniform coverage than brush painting and better overall catalyst-membrane adhesion. Various palladium loadings were attempted with a range from 2 to 12 mg cm⁻². In addition, palladium (up to 4 mg cm⁻²) was brush painted onto carbon cloth to form a gas diffusion electrode in some variations of the fuel cell assembly.

Variations on the mass ratio of AS-4 ionomer to catalyst were explored from a range of 1:3–1:12. Finally, the cathode gas was heated and humidified. We continue to use Pt black at the cathode in order to optimize the anode without introducing potential cathode limitations at this time.

2.2. Electrochemical cell

The electrochemical experiments were carried out in a standard three electrode glass cell as described previously but with the following modifications [13]. The reference electrode was a standard calomel electrode (CH Instruments) stored in saturated potassium chloride (0.244 V vs SHE).

3. Results and discussion

3.1. Optimization of the Direct Formate Fuel Cell

In order to optimize the DFFC using the materials at hand, we varied the anode catalyst loading (2–12 mg cm⁻²), location of anode catalyst (direct spray on membrane; brush paint on gas diffusion layer), and mass ratio of ink ionomer to catalyst (1:3–1:12). We determined the most efficient loading to be 4 mg cm⁻² spray paint on membrane, 4 mg cm⁻² brush paint on GDL, and 1:6 ionomer to catalyst ratio. The voltage–current plots from this loading combination are demonstrated in Fig. 1. This DFFC was operated with 1 M HCOOK anode fuel, oxygen as the oxidant, and the fuel cell operating at 60 °C. Addition of 2 M KOH was used in one of the DFFCs shown. The maximum power density of 267 mW cm⁻² for this first membrane electrode assembly (MEA1) is significantly greater than that of the recent DFFC reports in the literature [12,13]. When the KOH was removed from the fuel stream, the maximum power density decreased to 157 mW cm⁻². Even this power density achieved without KOH is 85% of the maximum power density reported to date for alkaline direct alcohol fuel cells at this temperature, but alcohol fuels require KOH added to the fuel stream to reach this level of performance [11]. The use of formate as a fuel therefore provides a key advantage in that KOH is not needed in the fuel stream to achieve competitive performance.

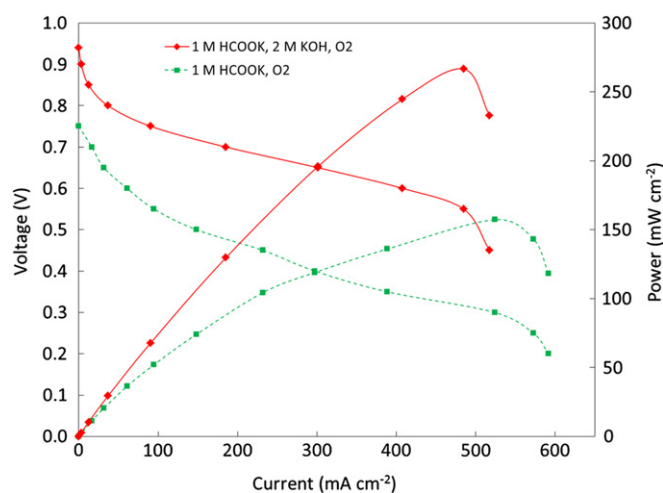


Fig. 1. VI plots demonstrating current and power densities at optimum conditions with 2 M KOH in fuel stream and without KOH in fuel stream. Power density of 267 mW cm⁻² is achieved with KOH and 157 mW cm⁻² is achieved without KOH. Fuel: 1 mL min⁻¹ 1 M HCOOK + 0 or 2 M KOH. Oxidant: 100 sccm humidified oxygen. Fuel cell temperature: 60 °C.

As expected, the performance of the DFFC decreases when air is used as the oxidant in the place of pure oxygen. The DFFC (MEA1) shown in Fig. 2 was operated using 1 M HCOOK anode fuel, air as the oxidant, and the fuel cell operating at 60 °C. Addition of 2 M KOH was also used in one of these fuel cells to produce a maximum power density of 167 mW cm⁻². Without KOH in the fuel stream, the power density decreased to 105 mW cm⁻². To our knowledge no one has yet reported an alkaline DLFC with a power density of this magnitude when air is used at the cathode and no KOH is added to the fuel stream.

It was determined that the optimum anode configuration was 4 mg cm⁻² spray painted on the membrane and 4 mg cm⁻² brush painted on the gas diffusion layer (MEA1). We also report two key findings when the DFFC was operated with 1 M HCOOK, 2 M KOH, and oxygen, which are summarized in Table 1 for comparison. First, we found that increasing the catalyst loading to 8 mg cm⁻² directly painted on the membrane and 4 mg cm⁻² on the GDL (MEA 2) only increased DFFC power density from 267 to 277 mW cm⁻². We find a 10% increase in power density at heavier loading when air is used as the oxidant. For the purpose of this report, we did not deem the minor addition of power density worth the increased catalyst loading; however, it may be advantageous for long-term fuel cell stability. We also found that only painting 8 mg cm⁻² directly on the membrane (MEA 3) without catalyst added to the GDL produced maximum power density of 219 mW cm⁻². Comparison of the performance of MEAs 1–3 suggests that significant performance enhancement comes from the brush painting of the GDL and that increasing catalyst loading in the spray painted membrane does not have significant impact beyond 4 mg cm⁻².

3.2. Dependence on temperature and fuel/KOH concentration

Direct liquid fuel cells utilizing either proton or anion exchange membranes are typically operated at a temperature elevated above ambient conditions in order to optimize performance. Over the past decade, the direct formic acid fuel cell (DFAFC) was shown to perform strongly at room temperature even though its competitor, the direct methanol fuel cell (DMFC) required elevated temperature [23]. In developing the DFFC, we had hoped to find that it would operate better than alcohols at lower temperature. However, we found that the power density decreased from 144 to 78 mW cm⁻² when the DFFC temperature was decreased from 60 to 40 °C [13].

Table 1

Summary of key fuel cell data for the DFFC using 1 M HCOOK. MEA1 contains 4 mg cm⁻² spray painted on the membrane and 4 mg cm⁻² brush painted on the GDL. MEA2 contains 8 mg cm⁻² spray painted on the membrane and 4 mg cm⁻² brush painted on the GDL; its performance is not significantly higher. MEA3 contains 8 mg cm⁻² spray painted on the membrane but not additional catalyst on the GDL. Its performance is weaker, indicating a significant advantage to GDL brush painting.

MEA #	Electrolyte	Oxidant	Maximum power density (mW cm ⁻²)	Current density (mA cm ⁻² @ 0.6 V)
1	2 M KOH	Oxygen	267	408
1	—	Oxygen	157	298
1	2 M KOH	Air	167	256
1	—	Air	105	80
2	2 M KOH	Oxygen	277	433
3	2 M KOH	Oxygen	219	339

Unfortunately, the application of these fuel cells in portable electronic devices would be strongest if the fuel cells can be optimized at or near ambient temperature. Fig. 3 shows our comparison of DFFC performance at various temperatures with 1 M HCOOK, 2 M KOH, and pure oxygen. We found that the DFFC performance decreased from 267 mW cm⁻² at 60 °C to 185 mW cm⁻² at 45 °C and 141 mW cm⁻² at 35 °C. It is interesting to note that the power density at 45 °C is competitive with the best reports of the DEFC at 60 °C. The conductivity of the membrane is expected to be temperature dependent; since alkaline membranes are still in a developmental stage, it is possible that this can be improved in the future. However, Jiang and Wieckowski show surprisingly strong temperature dependence for formate oxidation in alkaline media in an electrochemical cell, which suggests that at least some of what we observe in the DFFC can be directly related to the reaction rate and not entirely due to limitations of the membrane or other components of the fuel cell assembly [12]. Despite the limitations brought on by temperature, we report significant activity in the DFFC at lower temperatures which demonstrates the possibility of lower temperature applications for the DFFC.

In our previous work we found a fuel concentration dependence in which the optimum was 1 M HCOOK, but we only tested up to 3 M HCOOK. This was not a very promising result considering that significant improvements to overall fuel cell energy density can be realized by utilizing fuels in high concentration. In alcohol fuel cells

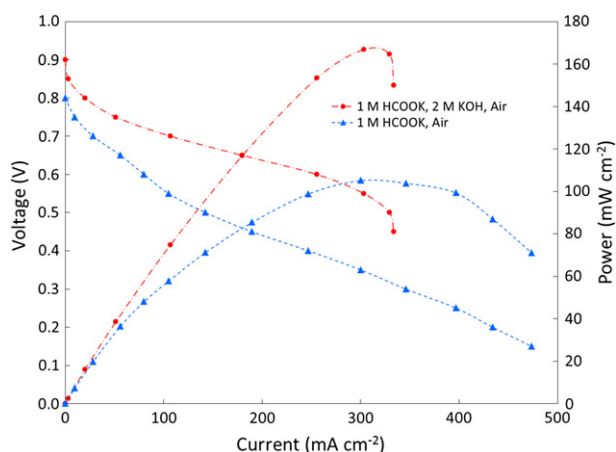


Fig. 2. VI plots demonstrating current and power densities when air is used at the cathode rather than pure oxygen. Power density of 167 mW cm⁻² is achieved with KOH and 105 mW cm⁻² is achieved without KOH. Fuel: 1 mL min⁻¹ 1 M HCOOK + 0 or 2 M KOH. Oxidant: 400 sccm humidified air. Fuel cell temperature: 60 °C.

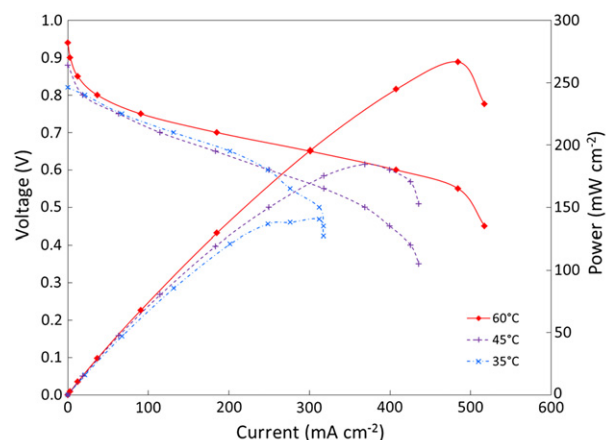


Fig. 3. VI plots demonstrating the effect of temperature on current and power densities under otherwise optimal conditions. The power density decreases from 267 to 185 mW cm⁻² when the temperature is decreased from 60 to 45 °C. The power density further decreases to 141 mW cm⁻² at 35 °C. Fuel: 1 mL min⁻¹ 1 M HCOOK and 2 M KOH. Oxidant: 100 sccm humidified oxygen.

using Nafion® membranes, crossover was a serious concern at high concentrations; although crossover effects are smaller in a formic acid fuel cell, it is still a concern at very high concentrations. A significant advantage of alkaline DLFCs is the difference in direction of electro-osmotic flow across the membrane, which minimizes crossover during fuel cell operation. An additional advantage specific to the DFFC is the extremely high solubility of potassium formate in water (39.4 mol kg^{-1} at 18°C) [24]. Therefore, it is highly desirable for DFFC optimization that the fuel concentration be as high as possible. We first examined the effect of potassium formate concentration in an electrochemical cell in 1–15 M HCOOK and 1 M KOH using 30 min chronoamperometry at -0.9 V vs SCE. As shown in Fig. 4, there is a consistent increase in current density with formate concentration. This confirms strong concentration dependence for the formate oxidation reaction. However, we did not observe this concentration dependence in the fuel cell in its current form. It will be important to the overall energy density of the fuel cell that we take advantage of the strong concentration dependence seen in Fig. 4. Therefore, future work will be carried out to improve fuel delivery and utilization at the anode while maintaining a high overall energy density in an alkaline environment.

Our previous work also showed a dependence on KOH concentration in the fuel stream; we showed that 2 M KOH was optimal, with lower and higher concentrations of KOH producing weaker fuel cell performance [13]. In this work, we used the electrochemical half-cell to determine whether this behavior was restricted to the fuel cell or specific to the oxidation of formate in alkaline conditions. We performed chronoamperometry in 1 M HCOOK and 0–3 M KOH at -0.9 V vs SCE, and the results are shown in Fig. 5. For the fuel streams containing KOH, the same trend that is observed in the fuel cell is evident in the half cell at short time periods (less than 5 min): 2 M KOH is optimal, while the higher and lower concentrations exhibit a slower rate of oxidation. This trend matches our fuel cell trend, since most of the fuel cell experiments were carried out at short time periods. However, beyond 5 min we observe a substantial increase in oxidation current in 3 M KOH, suggesting that some DFFC performance increase might be expected at longer time periods. However, the difference between 2 M and 3 M KOH is only about 10% after 30 min in the electrochemical cell, so the minor increase expected in DFFC performance would probably not be worth the additional alkaline required in the fuel stream. The results in Fig. 5 do confirm that the formate oxidation reaction is dependent on

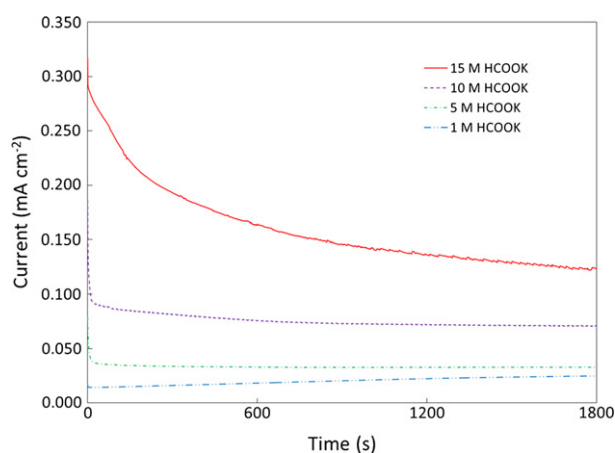


Fig. 4. Constant potential experiments in an electrochemical cell using a palladium black working electrode at -0.9 V vs SCE and rotating at 2000 rpm. As the formate concentration is increased from 1 to 15 M (with constant 1 M KOH electrolyte), the oxidation rate increases.

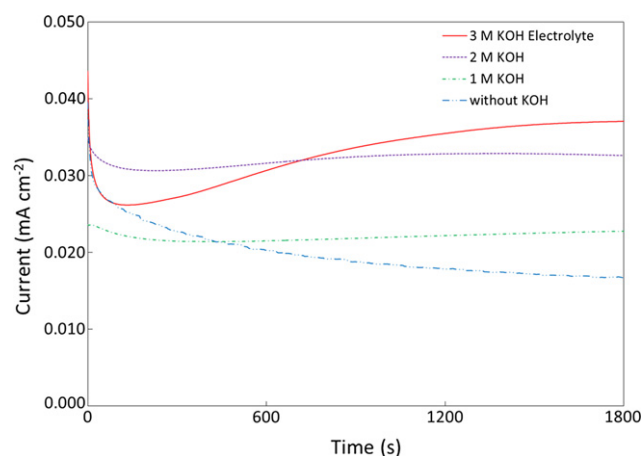


Fig. 5. Constant potential experiments in an electrochemical cell using a palladium black working electrode at -0.9 V vs SCE and rotating at 2000 rpm. As the hydroxide concentration is increased from 0 to 3 M (with constant 1 M HCOOK fuel), the oxidation rate beyond 5 min increases. However, at shorter time periods, 2 M KOH is the optimum concentration.

hydroxide concentration as suggested by the previously proposed mechanism: [17].



In ethanol electro-oxidation in alkaline media, the optimum hydroxide ion concentration was found to be 1 M, and ethanol requires adsorbed hydroxyl in its rate determining step [5]. However, adsorbed hydroxyl is not necessary for formate oxidation, and we find that optimal formate oxidation occurs when the hydroxide concentration is 2 M.

4. Conclusion

We demonstrate a significantly improved DFFC when the anode is optimized according to the procedures described in this report. We make several key points about alkaline DLFCs. First, the maximum power density of the DFFC was improved to 267 mW cm^{-2} , which is a very high power density for an alkaline DLFC operating under optimal conditions. We also show very competitive performance under preferred conditions (no KOH in the fuel and air as the oxidant): 105 mW cm^{-2} . We find that decreased temperatures decrease DFFC performance as expected. However, our anode still is not optimized for high concentrations of formate; our fuel cell performance does not match that of the electrochemical cell where we see increased oxidation rate with increased formate concentration. Now that the DFFC anode has been optimized, we expect to be able to move away from noble metal catalysts in the DFFC.

Acknowledgments

We would like to thank Kenji Fukuta (Tokuyama) for helpful discussions regarding operation of the alkaline membrane. We would like to acknowledge the support of this research by startup and intramural grant funds from California State University, Fullerton.

References

- [1] Y. Zhu, S.Y. Ha, R.I. Masel, *Journal of Power Sources* 130 (2004) 8.
- [2] E. Antolini, *Journal of Power Sources* 170 (2007) 1.
- [3] H.S. Liu, C.J. Song, L. Zhang, J.J. Zhang, H.J. Wang, D.P. Wilkinson, *Journal of Power Sources* 155 (2006) 95.
- [4] P.A. Christensen, A. Hamnett, D. Linares-Moya, *Physical Chemistry Chemical Physics* 13 (2011) 11739.
- [5] C. Bianchini, P.K. Shen, *Chemical Reviews* 109 (2009) 4183.
- [6] C. Bianchini, V. Bambagioni, J. Filippi, A. Marchionni, F. Vizza, P. Bert, A. Tampucci, *Electrochemistry Communications* 11 (2009) 1077.
- [7] Y.S. Li, T.S. Zhao, Z.X. Liang, *Journal of Power Sources* 187 (2009) 387.
- [8] V. Bambagioni, C. Bianchini, A. Marchionni, J. Filippi, F. Vizza, J. Teddy, P. Serp, M. Zhiani, *Journal of Power Sources* 190 (2009) 241.
- [9] E.H. Yu, U. Krewer, K. Scott, *Energies* 3 (2010) 1499.
- [10] J. John, H. Wang, E.D. Rus, H.D. Abruna, *The Journal of Physical Chemistry C* 116 (2012) 5810.
- [11] J.B. Xu, T.S. Zhao, Y.S. Li, W.W. Yang, *International Journal of Hydrogen Energy* 35 (2010) 9693.
- [12] J. Jiang, A. Wieckowski, *Electrochemistry Communications* 18 (2012) 41.
- [13] A.M. Bartrom, J.L. Haan, *Journal of Power Sources* 214 (2012) 68.
- [14] Y.S. Li, T.S. Zhao, *International Journal of Hydrogen Energy* 37 (2012) 4413.
- [15] Z.X. Liang, T.S. Zhao, J.B. Xu, L.D. Zhu, *Electrochimica Acta* 54 (2009) 2203.
- [16] E. Jacobsen, J.L. Roberts Jr., D.T. Sawyer, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 16 (1968) 351.
- [17] T. Takamura, F. Mochimaru, *Electrochimica Acta* 14 (1969) 111.
- [18] P. Taberner, J. Heitbaum, W. Vielstich, *Electrochimica Acta* 21 (1976) 439.
- [19] P.P. Hellsten, J.M. Salminen, K.S. Jorgensen, T.H. Nysten, *Environmental Science & Technology* 39 (2005) 5095.
- [20] T. Schaub, R.A. Paciello, *Angewandte Chemie International Edition* 50 (2011) 7278.
- [21] A.S. Agarwal, Y. Zhai, D. Hill, N. Sridhar, *ChemSusChem* 4 (2011) 1301.
- [22] T. Arai, S. Tajima, S. Sato, K. Uemura, T. Morikawa, T. Kajino, *Chemical Communications* 47 (2011) 12664.
- [23] S. Ha, R. Larsen, Y. Zhu, R.I. Masel, *Fuel Cells* 4 (2004) 337.
- [24] C. Balarew, T.P. Dirkse, O.A. Golubchikov, M. Salomon, *Journal of Physical and Chemical Reference Data* 30 (2001).